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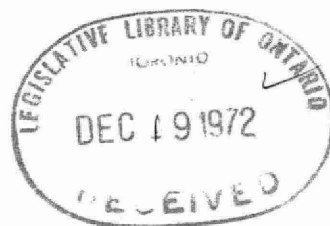
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TORONTO 195, ONTARIO

AN INVESTIGATION OF THE
PHOSPHATE RELEASE PROPERTIES OF CHEMICAL SLUDGES
PRODUCED DURING WASTE WATER TREATMENT

MINISTRY OF THE ENVIRONMENT

RESEARCH BRANCH



Research paper

May, 1972

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AN INVESTIGATION OF THE
PHOSPHATE RELEASE PROPERTIES OF CHEMICAL SLUDGES
PRODUCED DURING WASTE WATER TREATMENT

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May, 1972

Division of Research
Paper No. W2035

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Introduction

Phosphorus removal in conjunction with conventional or modified waste treatment processes is of prime significance in reducing the accelerated eutrophication of natural waters receiving waste water treatment plant effluents.

Phosphorus is an indispensable constituent of living tissues and plays an important role in the energy metabolism of organisms. Phosphorus in cells exists in the form of nucleic acid, nucleotides and inorganic phosphates. Also existence of mono- or polyphosphate is presumed in activated sludge floc. The high energy phosphate compound ATP (adenosintriphosphate) is produced through oxidation (respiration) of compounds such as carbohydrates, taking in many biosynthetic reactions.

The removal of phosphorus in the absence of any oxidizable material, either external substrate or internal storage products, requires that some other mechanism be involved besides the formation of ATP. The uptake may be associated with the physical adsorption of phosphorus with biological storage. Varma and Reid (1) speculated that microbial slimes remove phosphorus from solution by (a) adsorption on the surface of cells followed by (b) assimilation during biosynthesis. They found out that in the presence of an organic substrate there was an almost instantaneous adsorption of phosphorus (P^{32}) by the micro-organisms. The rate of phosphorus assimilation was observed to exceed that of adsorption after about six hours.

Factors affecting removal of phosphorus from sewage by sludge organisms with a view towards modifying aerobic and chemical sewage treatment processes to produce effluents with low phosphorus concentrations have been investigated by many authors, (2,3,4,5,6,7). One of the most successful ways is coagulation with a suitable cation followed by activated sludge treatment.

Shapiro et al (8) found, that although the concentration of soluble phosphate was reduced during aeration, the effluent from secondary sedimentation frequently contained higher concentrations of phosphate than did the effluent from the aeration tanks, indicating that a considerable amount of the phosphate taken up by the sludge was leaching out of the cells during sedimentation. In his original paper, Shapiro (9) stated that culture and mixed microorganisms are able to release a large proportion of their phosphorus to the medium in matter of hours when kept under anoxic conditions. Phosphorus is lost, probably as orthophosphate, and apparently mostly from the acid soluble fraction of cells and later from nucleic acids. The process is completely reversible upon aeration. After the aeration stage of activated sludge treatment which lasts 2 - 8 hours, the organisms are concentrated five to ten fold by settling and the high respiration rate rapidly depletes the oxygen in the mass of organisms with a resultant release of phosphate. Further experiments at different temperatures showed the phenomenon to be temperature dependent. Higher concentrations of phosphate in solution did not inhibit release and percentages of C, H, and N remained essentially unchanged.

The only systematic change was a slight increase in Kjeldahl nitrogen. The fact, that soluble phosphorus concentrations were essentially the same as the total phosphorus, indicated that phosphorus was being released either as orthophosphate or as an easily hydrolyzable compound. These results could be explained as the result of the reduction of substances such as ferric phosphate during anoxia, followed by its reformation during aeration. Rapid release occurs only when the redox potential has fallen to the voltage at which ferric iron would be reduced to the soluble ferrous state. The release is also stimulated by poisons of the cytochrome system such as KCN and HgCl_2 .

Experimental Procedure

In this investigation a series of laboratory experiments were carried out to study the phenomenon of the release of phosphorus from sludge produced in waste water treatment systems employing chemical processes for phosphorus removal.

Two vessels of 5 litre volume each were constructed of 3/8" Plexiglas; the smoothly cut Plexiglas pieces being permanently bonded with chloroform. Each vessel was equipped with a magnetic stirrer and a cover through which passed electrodes to measure redox potential, dissolved oxygen and temperature, a tube for bubbling in nitrogen or air and a siphon for sampling. The entire system was sealed to maintain controlled internal conditions. (See Figure 1).

During this investigation, sixteen experiments in all were performed, most of them associated with an experiment being carried out at the Newmarket WPCP.

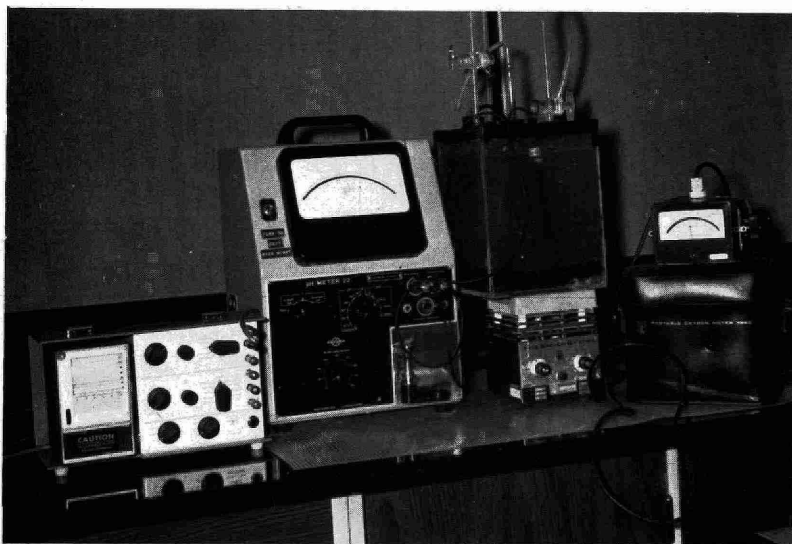


Figure 1

Model Plant and Ancillary Equipment

At the Newmarket WPCP a process has been designed into an existing 2.0 MIGPD conventional activated sludge plant whereby high levels of phosphorus removal are being attained. The process involves the addition of lime to the raw sewage in a rapid mix chamber with chemical coagulation and sedimentation subsequently taking place within the primary clarifiers. As well as removing high levels of phosphorus, the lime also considerably increases the efficiency of BOD and Suspended Solids removals within the primary clarifiers. The relatively weak primary effluent then passes on through the secondary treatment stage. The primary sludge, containing relatively small quantities of waste secondary sludge, is of a considerably different character than normal primary sludge because of the lime and requires special attention.

It was observed during the operation of this process that frequently the chemical sludge settled very poorly in the primary clarifiers. Although BOD removal levels remained fairly constant there was frequently a high carryover of suspended floc material containing as much as 4 to 5 mg/l Total Phosphorus but generally less than 1.5 mg/l Soluble Phosphorus. Experiments 1 to 4 were therefore aimed at determining the conditions influencing the fate of this chemically bound phosphorus carryover during the aeration and final settling processes.

In these experiments fresh samples of mixed liquor were settled in large containers for 10 minutes, the supernatant siphoned off and discarded, and the concentrated sludge of micro-organisms transferred to the test vessel in which the sludge was kept under the desired conditions.

The vessel contents were stirred by a magnetic stirrer and kept from further contact with air by nitrogen bubbling. Periodically, samples were withdrawn and filtered through glass fiber filter RA 934AH. Orthophosphate in the filtrate was determined by the stannous chloride method (10), modified for low phosphorus concentration determination. A DB Beckman Spectrophotometer was used at 690 wave length providing a light path of 4 cm. Absorbance was found to be linearly dependent on concentration of phosphorus in the range of 0 to 1.12 mg/l. Higher concentration showed a deviation from Lambert-Beer's law, and were carried out using the standard stannous chloride method. All determinations were made in duplicate. All phosphorus and phosphate values are reported as P.

Subsequent experiments were carried out in much the same manner, with the duration of the experiment influenced by the conditions of study.

Experiments 6 to 14 were carried out using the raw primary sludge from the Newmarket phosphorus removal installation. Experiment No. 5 employed primary sludge from the Barrie WPCP, obtained during an extended test period when alum was being fed into the aerated grit tank at the head of the conventional activated sludge plant for phosphorus removal purposes.

Experiments 6 to 9 were carried out to investigate the conditions affecting phosphate release from primary sludges containing levels of Total Phosphorus as high as 1800 mg/l P.

Experiments 10 to 14 covered another area of investigation to determine the ability of polyelectrolytes to inhibit the release of phosphate from the Newmarket primary lime sludge.

In these investigations two reaction vessels were used in parallel; one acting as a control while the polyelectrolyte was added to the second. Tests were carried out using the anion-active polyelectrolyte "Purifloc A23" in concentrations of 1, 2 and 4 mg/l and with "Sodium Alginate" also an anion-active polyelectrolyte in concentrations of 1 and 6 mg/l.

A further set of experiments, 15 and 16 involved observations of the release of phosphate from the mud of a lake previously treated with alum to effect the precipitation of extremely high concentrations of algae.

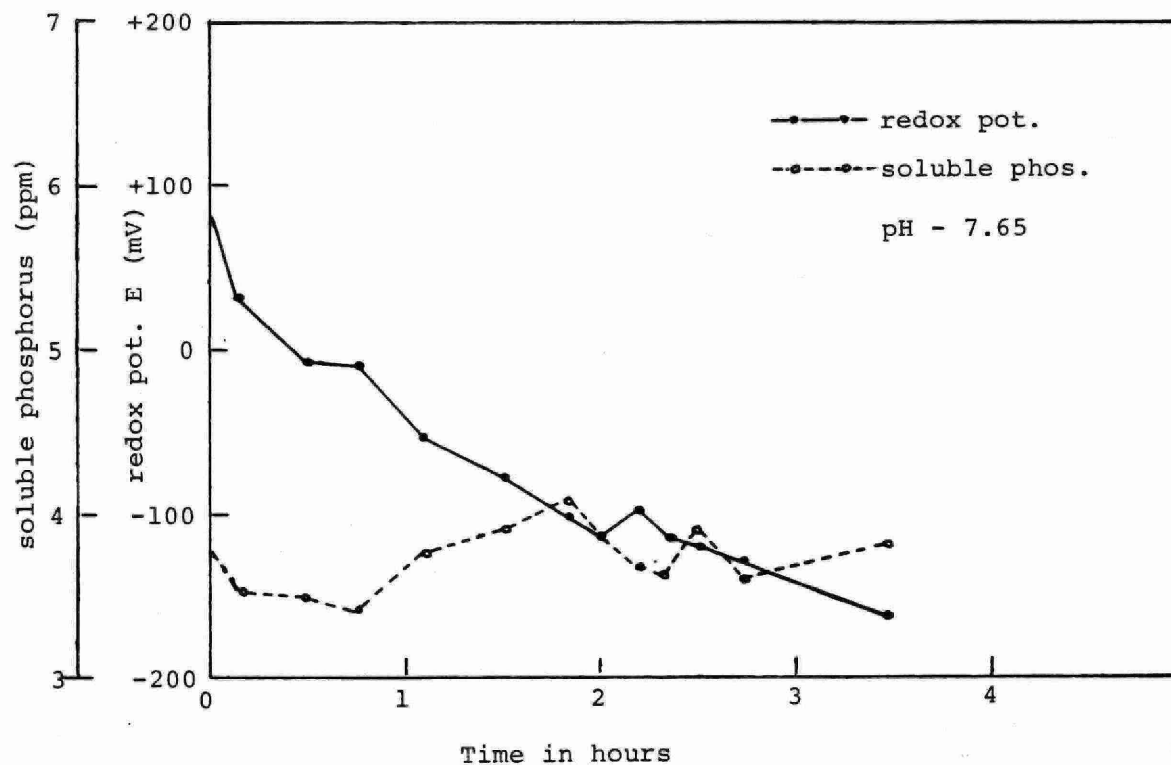
Observations

Figures 2 and 3 represent results of the laboratory investigations directed at determining whether or not the lime reaction products, carried over into the aeration section of the Newmarket WPCP, entered into solution under anaerobic or aerobic conditions.

Contrary to the statement by Shapiro and Levin (8), release did not occur during the first four hours under anaerobic conditions. (See Figure 2). Later phosphate release seemed to be dependent upon the redox potential (Figure 3) as the concentration of dissolved phosphate increased from an initial value of 3 ppm to 23 ppm in 12 days without any change in pH.

After 12 days under anoxic conditions, air was bubbled through the culture and the soluble phosphate was taken back up from solution at a rate much more rapid than it had been released.

Experiment No. 5 using the Barrie WPCP primary alum sludge

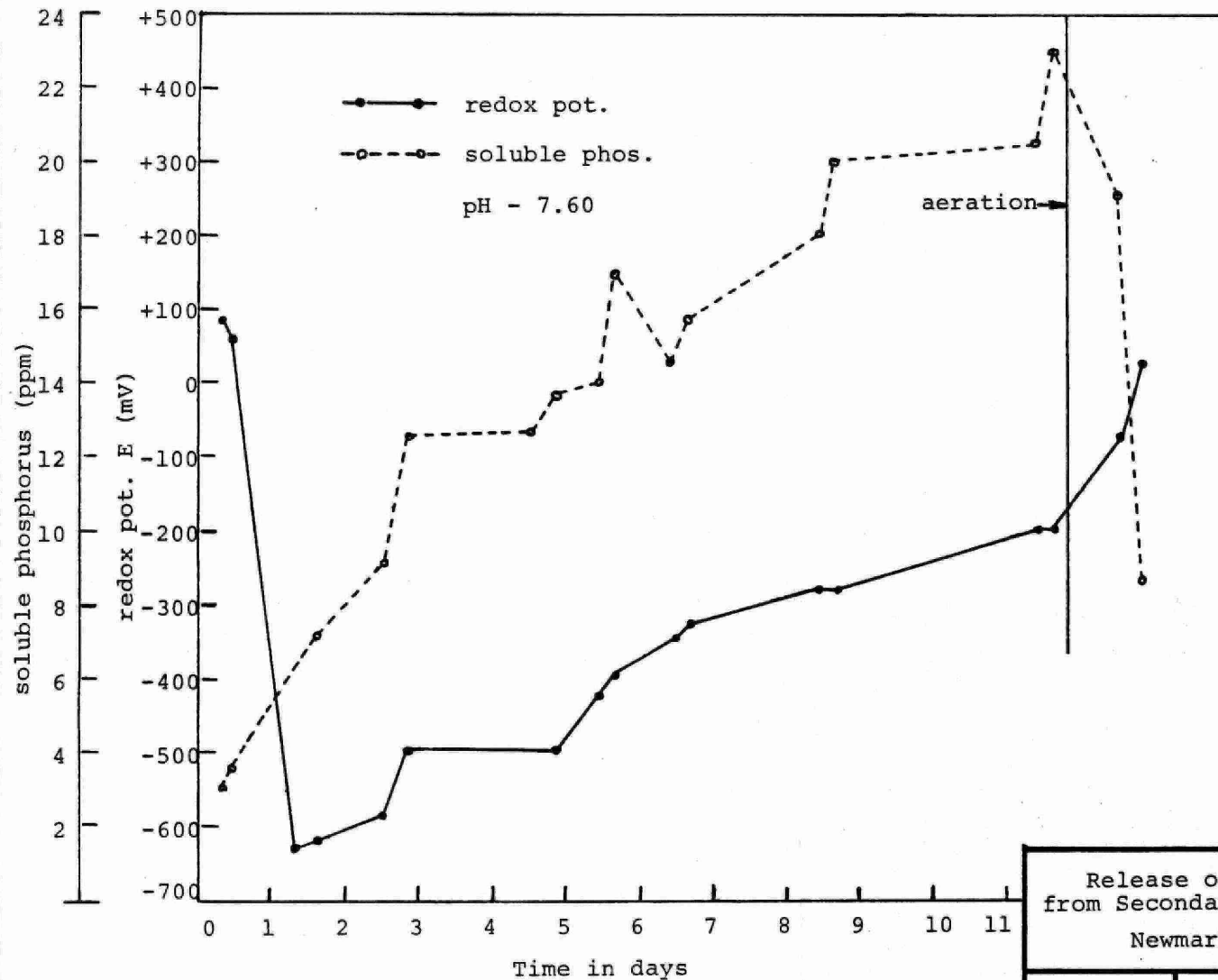


Release of Phosphate
from Secondary Lime Sludge
Newmarket WCPC

Fig. 2

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Release of Phosphate
from Secondary Lime Sludge
Newmarket WPCP

Fig. 3

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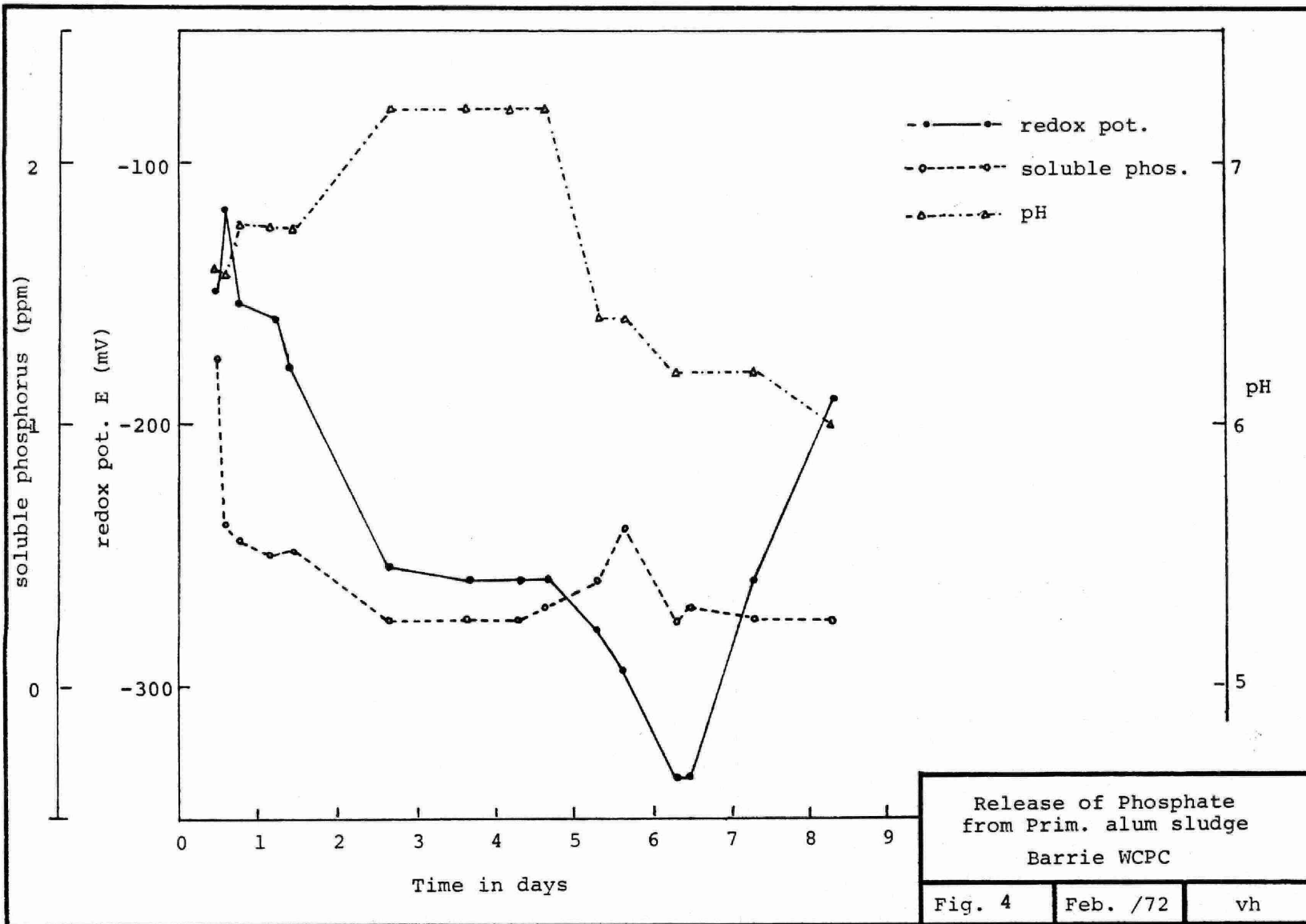
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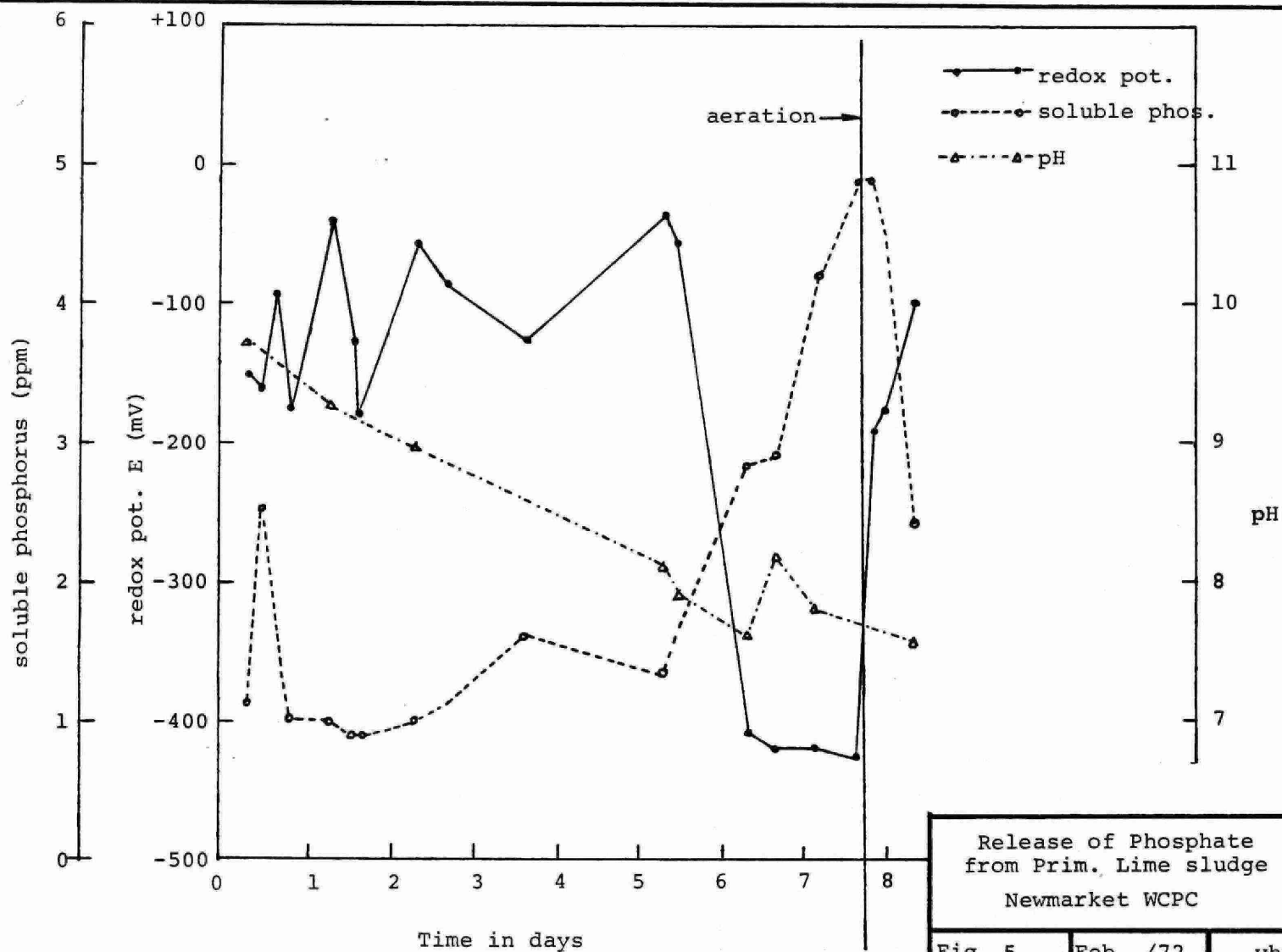
indicated positively no release of phosphate (see Figure 4) from the sludge held under anoxic conditions for a period of 8 days, even through the redox potential dropped considerably and the pH decreased from 6.6 to 6.0 .

Results of experiments 6 to 9 using the Newmarket WPCP primary lime sludge are presented in Figures 5,6,7, and 8. In these experiments, the release of phosphate, determined to be orthophosphate, was found to be directly related to a decrease in pH and to a decrease in redox potential. Again, aeration of the sludge reversed the phosphate release reactions and the phosphate was rapidly taken out of solution. In all cases the pH decreased from above 9 to 7.5 in a period of 7 to 8 days.

Figures 9, 10 and 11 present the results of experiments 10, 11 and 12 to determine the effect of the anionic polyelectrolyte Purifloc A23 on the release of phosphate from the Newmarket primary lime sludge. All concentrations of the polyelectrolyte tested significantly repressed the release of phosphate as compared to the control. Although some release still occurred in all cases, this release was again reversible upon aeration. (See Figure 11).

The results of experiments 15 and 16 are presented in Figures 12 and 13 which dramatically show the effect of oxygen on the release of phosphate from lake bottom muds. In experiment No. 15 release of phosphate occurred immediately after the redox-potential had dropped below -100 mV, during which time the oxygen concentration also dropped from 1.7 mg/l to zero. In experiment No. 16, where the mud stayed aerobic for a longer period of time, there was no release of phosphate from solution.



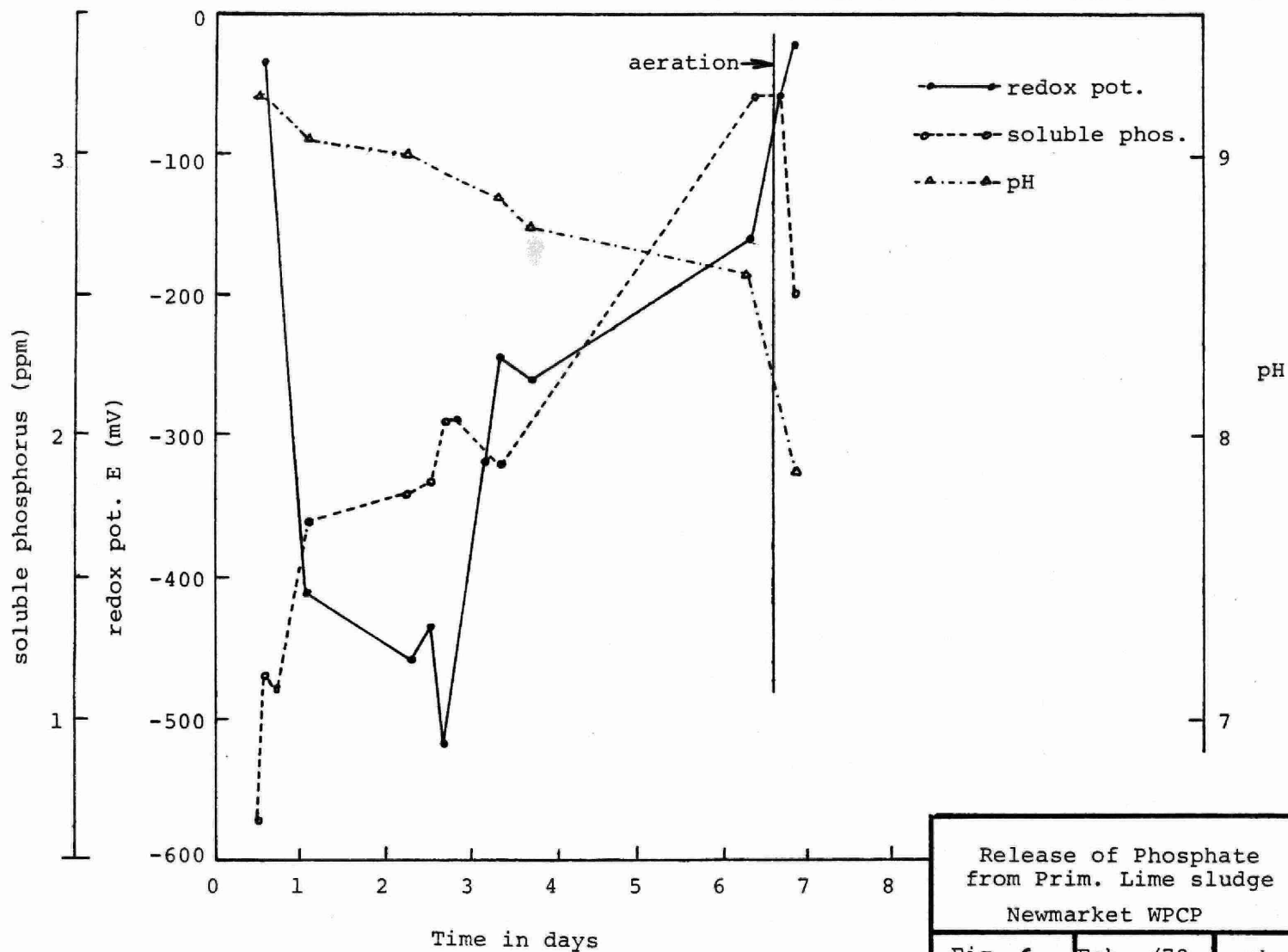


Release of Phosphate
from Prim. Lime sludge
Newmarket WCPC

Fig. 5

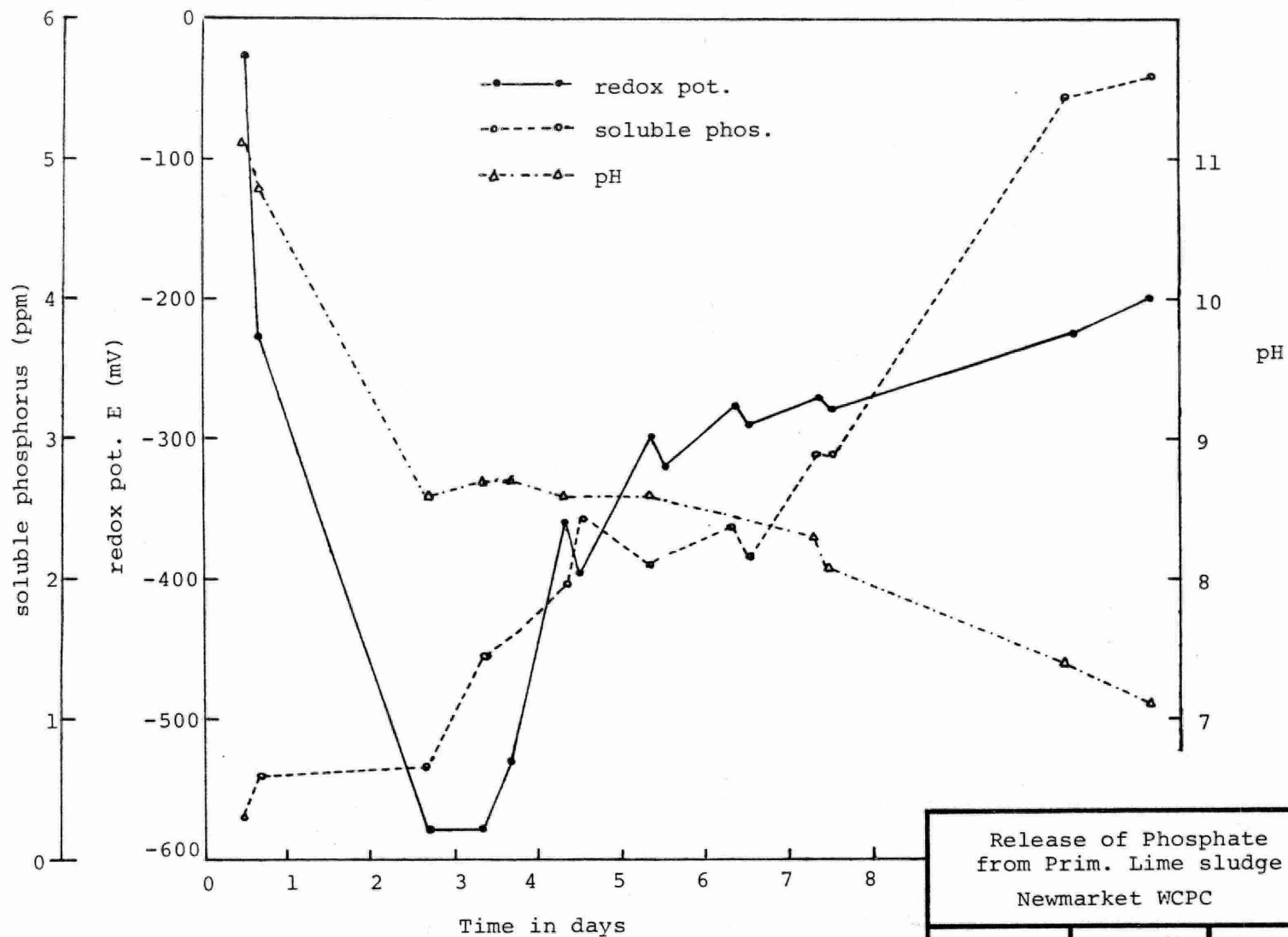
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Release of Phosphate
from Prim. Lime sludge
Newmarket WPCP

Fig. 6	Feb. /72	vh
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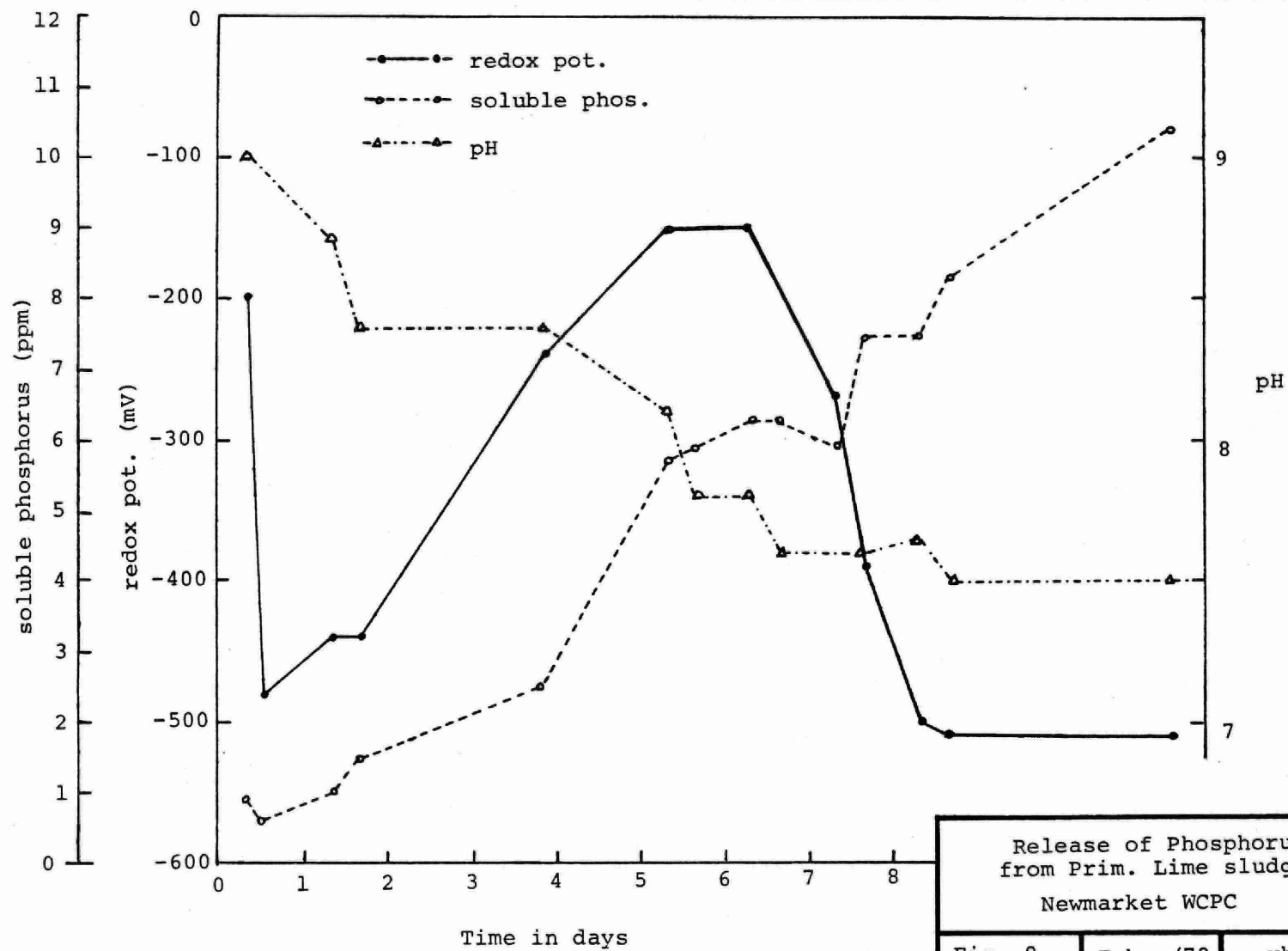


Release of Phosphate
from Prim. Lime sludge
Newmarket WPCP

Fig. 7

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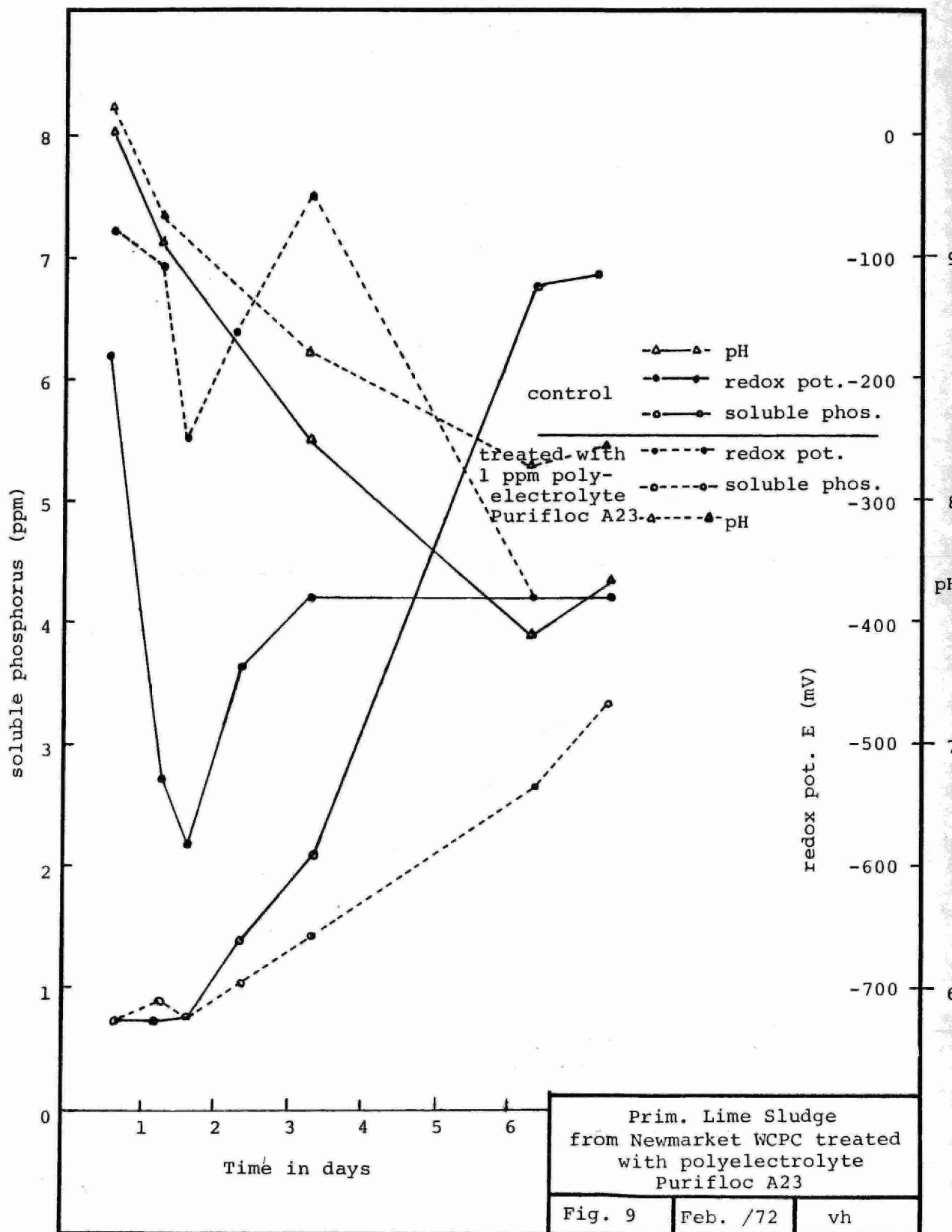


Release of Phosphorus
from Prim. Lime sludge
Newmarket WPCP

Fig. 8

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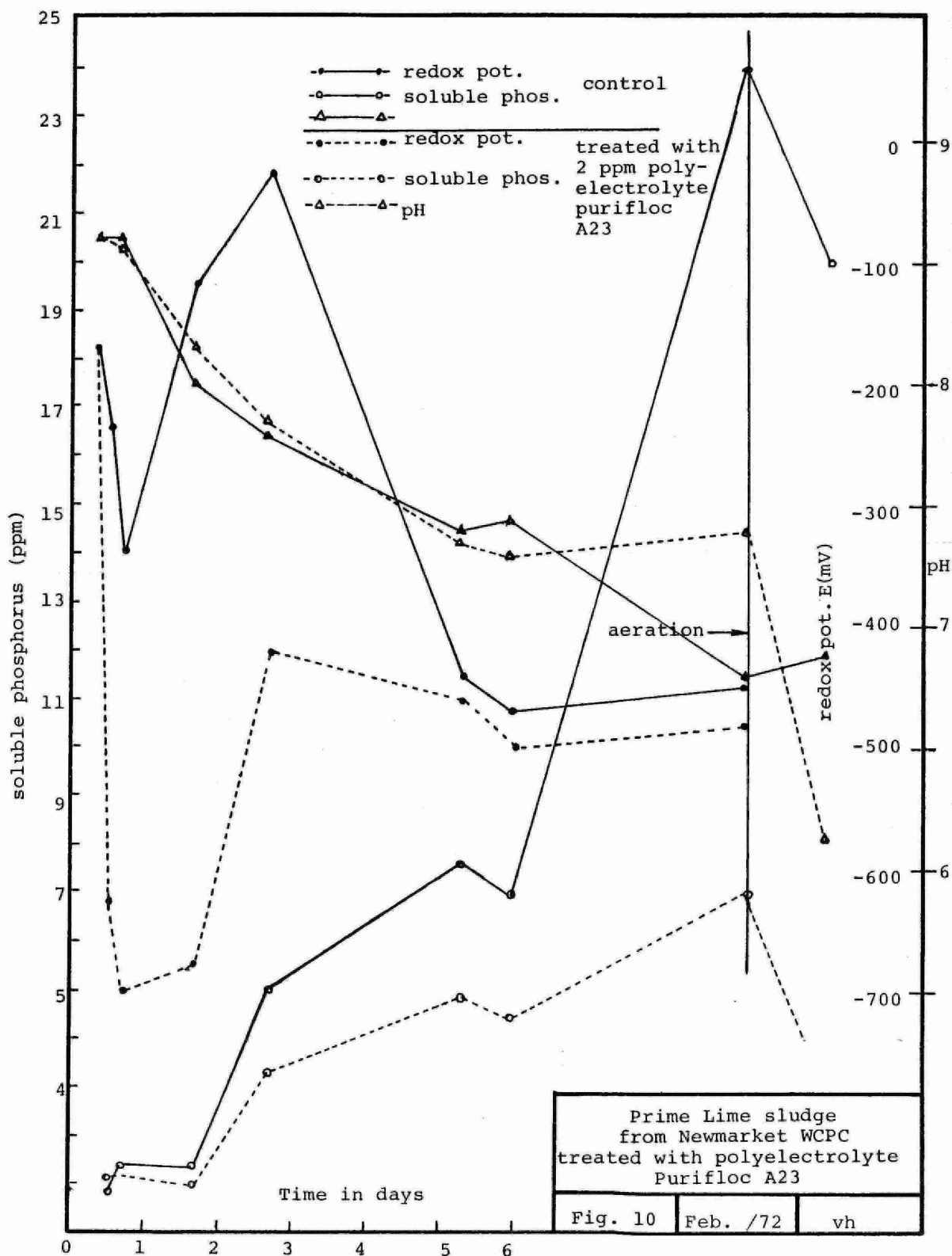


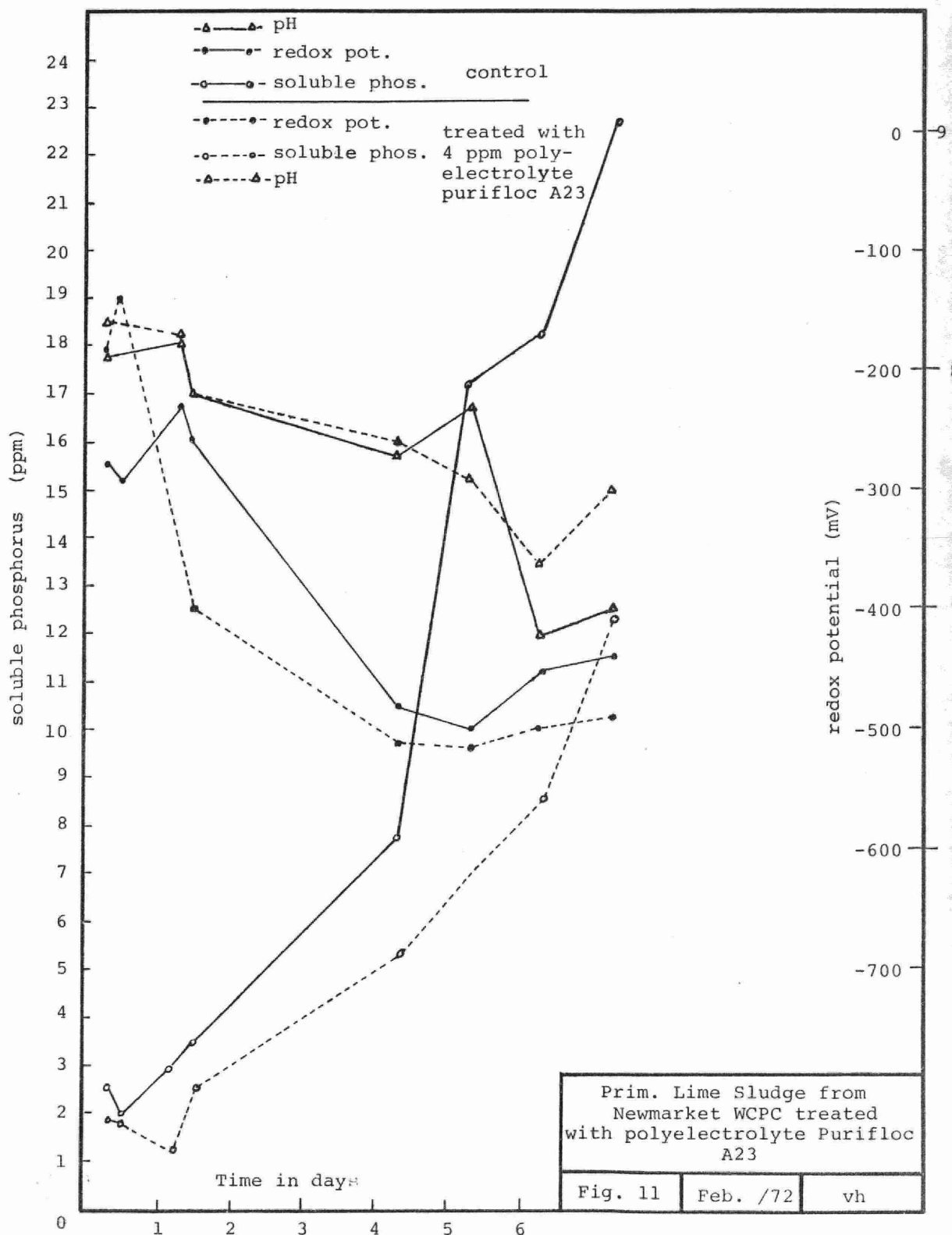
Prim. Lime Sludge
from Newmarket WPCP treated
with polyelectrolyte
Purifloc A23

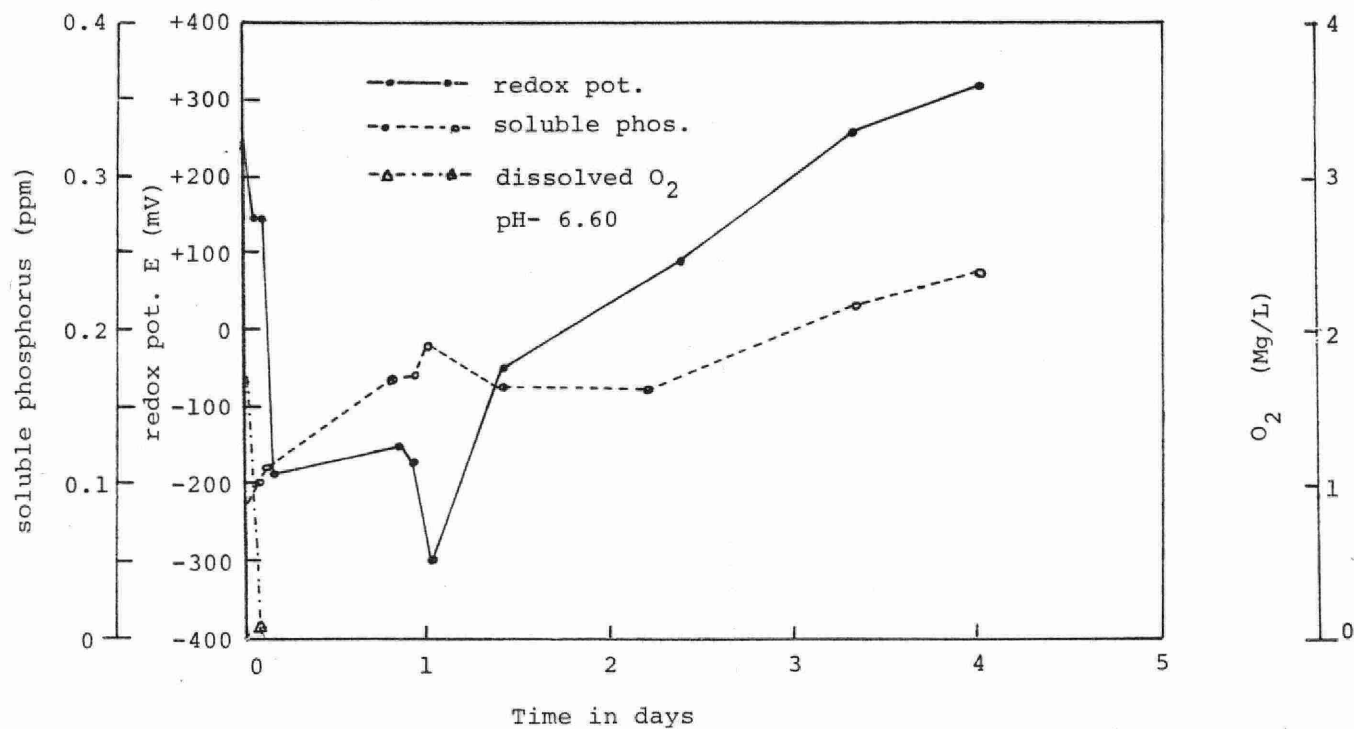
Fig. 9

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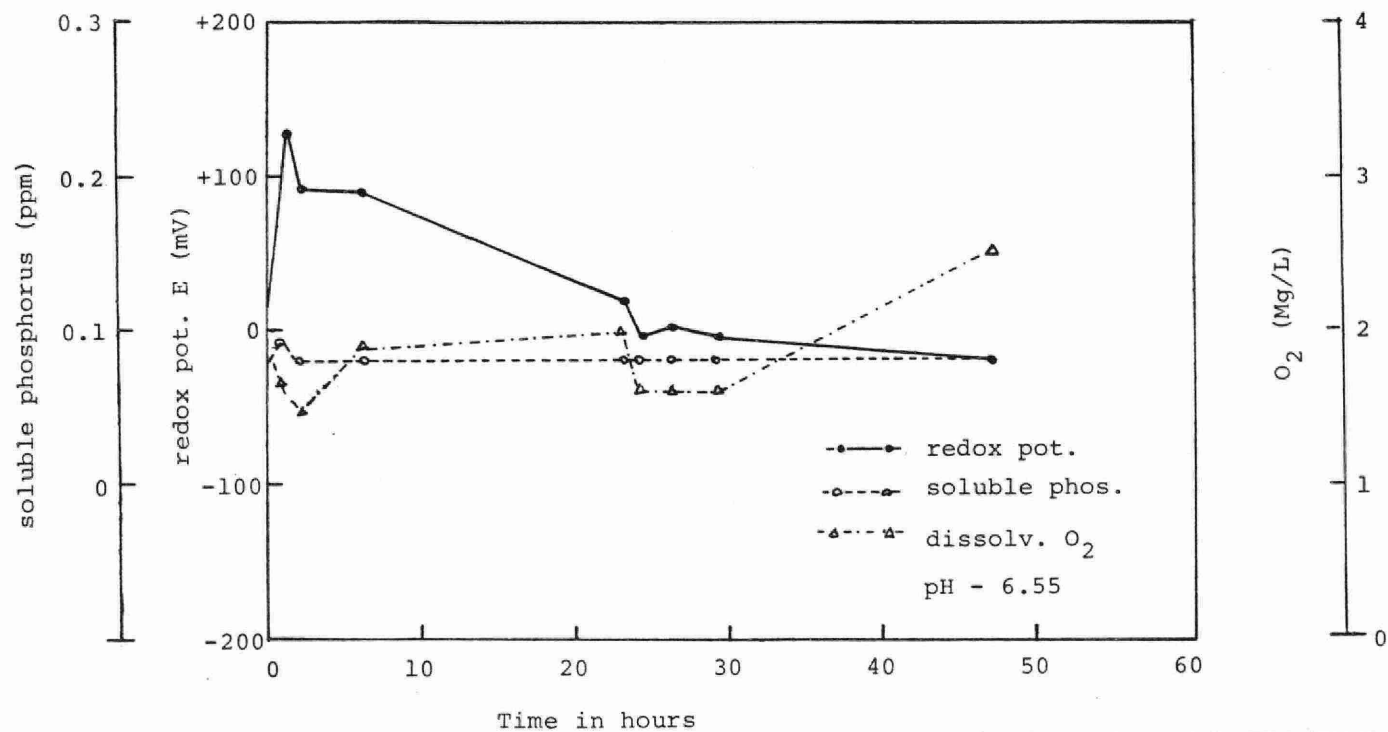


Release of Phosphate
from mud
Newmarket WPCP

Fig. 12

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Release of Phosphate
from mud

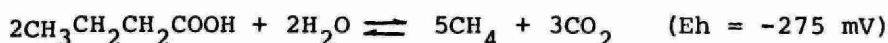
Fig. 13

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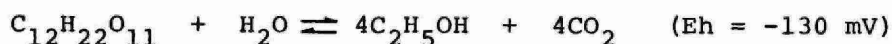
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Discussion

It is well known that in aquatic life as well as in the self-purification of polluted waters and, especially in biological sewage treatment, oxidation-reduction processes play an important role. One example is the anaerobic sludge digestion reaction:



or in the fermentation of suspensions,



If phosphate is precipitated by Fe^{III} , and since the redox potential reaction

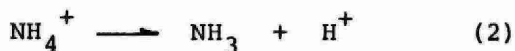
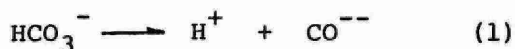


Fe^{III} in FePO_4 must be reduced before sulfate reduction and methane fermentation are thermodynamically possible. The valence of Fe^{III} would prevent CH_4 fermentation. The reduction of Fe^{III} to Fe^{II} is accompanied by the release of phosphate (H_2PO_4^- , $\text{HPO}_4^{=}$) to solution.

Delay of release of phosphate in experiments 1, 2 and 4 under anaerobic conditions probably was due to the different character of lime-treated sludge. Phosphate bonded to calcium as hydroxyapatite ($\text{Ca}_5\text{OH}(\text{PO}_4)_3$) is thermodynamically stable but its solubility is a function of pH and the complex is very insoluble only at alkaline pH. Under acidic conditions even at the neutral pH of anaerobic digesters, formation of the more soluble forms

mono-calcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) and di-calcium phosphate ($\text{Ca}_2\text{H}_2(\text{PO}_4)_2$) occurs. Presence of calcium in digesters does not make any noticeable change in redox potential. But it is well established that bacteria can use particulate phosphorus in a microzone surrounding the cell and that the element may be passed on through food chains involving protozoan or crustacean intermediaries. Increased solubility of strongly basic phosphates may be the result of base exchange from the local acid products of decomposition.

In all experiments related to primary sludge, pH values of the sludge dropped off during 6-7 days to 7.5 from different initial points, mostly over 9. This can be explained on the basis of neutralization through organic acids and the insufficient presence of buffer solutions (NH_4HCO_3) created from decomposition of glycid, fats and proteins (CO_2) and aminoacids (NH_3). Ammonium bicarbonate (NH_4HCO_3) is known as a regulator of pH and plays a very important role in biological decomposition of organic compounds and in lime precipitation of waste water. The buffer capacities (equations 1 and 2) controlled the pH after lime addition by neutralizing the hydroxide ions from the calcium hydroxide (11),



It was also determined that breakdown of aluminum phosphate complexes at normal digester pH is almost negligible. Similar results were obtained by Mulbarger and Shifflet (12); these being

contrary to Jarebo, who in his Ph.D. work (13) stated that using aluminium, a certain amount of complex phosphorus went back to solution under anaerobic conditions.

Results of these experiments were substantiated by field observations. The fact, that no increase of soluble phosphorus occurs during anaerobic digestion can not be simply explained. Possibly it is connected with the coating of colloids on the microbial cells or to precipitation of biologically released phosphorus by unreacted aluminum.

It is also possible to state, that polyelectrolyte Purifloc A23 can partly inhibit release of phosphate under anaerobic conditions. 1 ppm Purifloc A23 accomplished a 47.7% reduction in the release of phosphate; 2 ppm - 70.7%; 4 ppm - 45.5% . Jarebo (13) during preparation of the reaction product calcium phosphate used a different type of polyelectrolyte and this did not prove to have any effect on the release of phosphorus from the precipitate. Therefore our observation can not be explained on the basis of chemical precipitation mechanisms only. Special conditions around the microcells must also be considered. Results from Marshall's Masters Thesis (14) substantiated our conclusions. To reduce the release of phosphate, he used the addition of Na_2SO_4 and MgSO_4 containing chemically bound oxygen to raise the redox potential. Sodium sulfate salt had no effect upon orthophosphate release but solution magnesium sulphate accomplished 46% reduction, presumably by a reduction of cell lysis rather than redox potential manipulation.

Conclusions

The studies reported herein give rise to the following conclusions. Although good phosphorus removal may be consistently achieved with the use of lime in many existing waste water treatment plants, it may be released back to solution if anoxic conditions are allowed to exist.

Disruption of microbial cells is the major cause of phosphate release. During the decomposition of biomass, through predominantly metabolic processes, the pH of the solution is reduced. This lowering of pH may result in the formation of the more soluble forms of calcium phosphates ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), $(\text{Ca}_2\text{H}_2(\text{PO}_4)_2)$ and therefore the release of phosphate must not necessarily be attributed to metabolic reactions alone.

The instability of calcium phosphate reaction products under anaerobic conditions leads to the conclusion that such compounds should not be allowed to directly or indirectly enter receiving waters, because they would immediately sink to the bottom where oxygen is depleted. At this point phosphorus would be released back to the water and be distributed to other parts of the lake during overturn.

Phosphorus is bound in lake sediment by different mechanisms; a) assimilated into organic matters, b) as an iron phosphate extractable with sodium hydroxide, c) tightly bound form probably occurring as aluminium phosphate and, d) as a more loosely bound form which is independent of the aluminium content of the sediment and can be removed by extraction with water. The ability of the sediment to absorb considerable amounts of the loosely bonded phosphorus means that large influxes of phosphorus into a lake may

be held temporarily and subsequently released to growing plants and algae.

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